

# PATENT SPECIFICATION

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## (54) COPOLYMERS AND THEIR USE IN THE TREATMENT OF MATERIALS

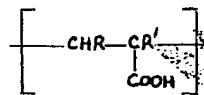
(71) We, ENGLISH CLAYS  
LOVERING POCHIN & COMPANY  
LIMITED, a British Company, of John Keay  
House, St. Austell, Cornwall, do hereby de-  
clare the invention, for which we pray that a  
patent may be granted to us, and the method  
by which it is to be performed, to be particu-  
larly described in and by the following state-  
ment:—

10 This invention relates to a deflocculation  
process and deflocculant compositions based  
on certain copolymers and, more particularly  
but not exclusively, is concerned with such a  
process and such compositions suitable for use  
15 in the treatment of particulate materials, in-  
cluding minerals such as kaolinitic clays and  
calcium carbonates.

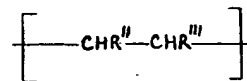
In certain industries, for example the clay  
industry, it is important to be able to defloc-  
20 culate mineral particles. This can be achieved  
by treating flocculated mineral particles,  
usually in the form of an aqueous slurry, with  
a deflocculant. Organic polymers have been  
used, heretofore, as deflocculants for kaolinitic  
25 clays and calcium carbonates and have advan-  
tages over inorganic deflocculants, such as  
tetrasodium pyrophosphates, in that they give  
slips whose viscosity changes little with time  
and which do not thicken when mixed with  
30 certain latices to make paper coating com-  
positions, sometimes known as coating colours.  
Hitherto, however, the high cost of commer-  
cially-available polymeric organic deflocculants  
has precluded their use in a number of fields  
35 where deflocculation of mineral particles is  
important, for example in the refining of  
kaolinitic clays.

According to one aspect of the present in-  
vention, there is provided a process for de-  
floc-  
40 culating a particulate material, which com-  
prises adding to a slurry of the particulate  
material a copolymer, or a water-soluble de-  
rivative of a copolymer, having a number  
average molecular weight in the range of from  
45 700 to 10,000 which contains from 30 to 95  
molar per cent of a first repeating unit having

the general formula



where R is hydrogen, a lower alkyl group, a  
carboxylic acid group or a lower alkyl carboxy-  
late ( $-\text{COOAlk}$ ) group and R' is hydrogen  
or a lower alkyl group; and from 70 to 5  
molar percent of a second repeating unit  
having the general formula



where R'' is hydrogen or a lower alkyl group  
and R''' is chlorine, a lower alkyl carboxylic  
ester ( $-\text{OCOAlk}$ ) group, or a lower alkyl  
carboxylate ( $-\text{COOAlk}$ ) group.

The term "lower alkyl" is used herein to  
mean a saturated radical containing up to 3  
carbon atoms; the preferred lower alkyl groups  
are methyl and ethyl.

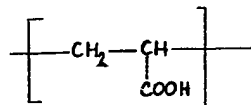
We have found that the copolymers speci-  
fied above or derivatives thereof, such as their  
water-soluble salts, e.g. the sodium, potassium  
and ammonium salts, or their water-soluble  
esters or partial esters, can be used either  
alone or admixed with other deflocculants,  
e.g. inorganic deflocculants, in a deflocculating  
composition for the treatment of, for example,  
aqueous slurries of particulate materials, e.g.  
of pigments. The invention accordingly also  
provides a deflocculating composition which  
includes a copolymer or copolymer derivative  
as set forth above.

It has also been found that the stability,  
with respect to viscosity change with time, of  
a kaolinitic clay slip deflocculated with an in-  
organic deflocculant such as tetrasodium pyro-  
phosphate and a deflocculating composition of  
the invention containing a small amount of a  
copolymer or copolymer-derivative as specified

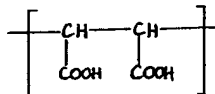
above is superior to that of a slip deflocculated with an inorganic deflocculant alone. This property is retained when synthetic latices, used in the preparation of coating colours, are added to the clay slips.

It has further been found that calcium carbonate minerals can be ground, by ball-milling or by sand-grinding, as slurries having a high solids content and containing a deflocculating composition of the present invention.

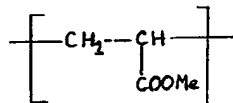
Advantageous copolymers are those in which the group R is hydrogen, a methyl group, a carboxylic acid group or a methyl carboxylate group; R' is hydrogen or a methyl group; R'' is hydrogen; and R''' is chlorine, a methyl carboxylate group or an acetate group. The first repeating unit may advantageously have the formula



or



and the second repeating unit may advantageously have the formula



Generally, one or more of the monomers employed to prepare the copolymer will itself contain a carboxylic acid group. In certain instances, however, one or more of the monomers can contain a group which can be converted to a carboxylic acid group after the polymerization of the monomers has been effected; for example, acrylonitrile or maleic anhydride can be used as one of the monomers, after which the nitrile or anhydride groups can be converted to carboxylic acid groups by hydrolysis.

Monomers which may be used in the preparation of the copolymers include vinyl acetate, vinyl chloride, maleic anhydride, acrylic acid, methacrylic acid and acrylonitrile; preferred monomers are maleic anhydride, acrylic acid and vinyl acetate.

The copolymers used in the present invention should contain at least sufficient acid groups to render them water-soluble. This is usually of the order of 30% by molar proportions in the copolymers.

Preferably, the copolymers have a number average molecular weight in the range of from 1,000 to 5,000 and have a narrow molecular weight distribution so that very little material of molecular weight below 500 or above 4,000 is present.

Particulate solids, for example kaolinitic clays, calcium carbonate minerals, and mixtures of kaolinitic clays and calcium carbonate minerals, can be deflocculated by dispersing throughout a slurry of the particles a deflocculating composition of the invention containing from 0.01 to 0.5% by weight, based on the dry weight of mineral to be deflocculated, of an organic copolymer or copolymer-derivative as set forth above. If the active component of the deflocculating compositions of the invention consists of a copolymer or copolymer-derivative as set forth above, the active component will generally be used at a dose rate of about 0.3% by weight of the dry mineral to be deflocculated, whilst considerably smaller quantities of the copolymer or copolymer-derivative may be present when used in conjunction with an inorganic deflocculant.

The copolymers set forth above can be prepared by a free-radically initiated polymerisation reaction carried out at a steady temperature, preferably in the range of from 50 to 135°C, and more preferably in the range of from 80°C to 120°C, in a non-reacting solvent. Temperature in excess of 135°C, or which vary during the reaction, are undesirable because of the likelihood of the products having an undesirable molecular weight range or distribution.

The following Examples illustrate the preparation of several copolymers of the type set forth above and their use as deflocculants in accordance with the invention.

#### EXAMPLE 1.

A copolymer of vinyl acetate and acrylic acid was prepared by simultaneously adding to a vessel containing isopropyl alcohol at 80°C (i) a solution in acetone of 100 grams of an equimolar mixture of a vinyl acetate and acrylic acid, and (ii) a solution in acetone of 1 gram of a 70% by weight aqueous dispersion of benzoyl peroxide. The solution was stirred throughout the period of the additions, which lasted for at least 50 minutes. The isopropyl alcohol was then either steam-distilled off and more water was added to the vessel, thereby giving an aqueous solution of the copolymer, or evaporated off to give a dry polymer product which was then re-dissolved in water. The copolymer solution, which was a transparent, colourless solution, was then cooled to room temperature. The yield of copolymer, found from several preparations, was between 60 and 80%. Titration of the copolymer with sodium hydroxide showed that the molar ratio of acrylic acid units to vinyl acetate units was 1.72:1, i.e. the copolymer containing 63.2 molar percent of the first repeating unit and 36.8 molar percent of the second repeating unit. The number average molecular weight of the polymer, as determined by isothermal distillation using a vapour pressure osmometer, was 3,800.

## EXAMPLE 2.

An equimolar mixture of vinyl acetate and maleic acid (as the acid anhydride) totalling 100 grams was dissolved in a mixture of xylene and acetone. The resulting solution was added to xylene at 100°C simultaneously with the addition thereto of a solution in acetone of one gram of an aqueous dispersion containing 70% by weight benzoyl peroxide. The solution was stirred throughout the period of the additions, which lasted for at least 55 minutes and which were performed under an atmosphere of nitrogen. The copolymer precipitated out from the xylene as a finely divided pale pink powder. The yield of copolymer, as determined from several batches, varied from 80—85%. The copolymer was then filtered, dried and dissolved in a warm aqueous solution of sodium hydroxide, which caused the hydrolysis of the anhydride groups in the copolymer chain to give carboxylic acid anions. The vinyl acetate-maleic acid copolymer was thus dissolved in water as the sodium salt.

Titration of several batches of the dried copolymer with sodium hydroxide showed that the ratio of vinyl acetate units to maleic acid units varied from 1.02:1 to 1.46:1, i.e. the molar percent of the first repeating unit in the polymer varied from 40.5 to 49.5, and that of the second repeating unit varied from 59.5 to 50.5. The number average molecular weight of the polymers varied from 1,200 to 2,300. Fractional precipitation of the copolymer showed that a wide molecular weight distribution was obtained. Polymer fractions having number average molecular weights of from 150 to 4,000 were obtained.

## EXAMPLE 3.

A copolymer of vinyl acetate and maleic acid was prepared as in Example 2, except that the acetone used to dissolve the aqueous suspension of benzoyl peroxide was replaced by xylene and the water contained in the benzoyl peroxide suspension was separated and removed from the solution. The copolymer precipitated out from the xylene as a finely divided white powder. The yield of copolymer was 92%. The copolymer was then treated as described in Example 2 so that a solution of the sodium salt in water was obtained.

Titration of the dried copolymer with sodium hydroxide showed that the ratio of vinyl acetate units to maleic acid units was 1.18:1, i.e. the copolymer contained 45.9 molar percent of the first repeating unit and 54.1 molar percent of the second repeating unit. The number average molecular weight of the polymer was 1,650. Fractional pre-

cipitation of the copolymer showed that the molecular weight distribution was more narrow than that obtained in Example 2, and the copolymer contained less low molecular weight material. Polymer fractions having number average molecular weights of from 960 to 3,000 were obtained.

## EXAMPLE 4.

An equimolar mixture of vinyl acetate and methacrylic acid totalling 100 grams was dissolved in toluene. The resulting solution was added to toluene at 110°C simultaneously with the addition thereto of a solution in toluene of benzoyl peroxide. The solution was stirred throughout the period of the additions which lasted for at least 70 mins. The copolymer precipitated out from the toluene as a finely divided white powder. The yield of copolymer was 99%. The copolymer was then dried and dissolved in an aqueous solution of sodium hydroxide. The vinyl acetate-methacrylic acid copolymer was thus dissolved in water as the sodium salt. Titration of the dried copolymer with sodium hydroxide showed that the ratio of vinyl acetate units to methacrylic acid units was 1:1, and the number average molecular weight of the copolymer was within the range 700 to 10,000 namely 2,000.

## EXAMPLE 5.

The sodium salts of copolymers prepared in Examples 1 to 4, together with a vinyl chloride-acrylic acid copolymer which had a molar ratio of acrylic acid units to vinyl chloride units of 10:1 and a number average molecular weight of 1700, were tested as deflocculants for a kaolinitic clay containing 70% by weight of particles smaller than 2 microns, 0.7% by weight of particles larger than 10 microns, and 0.03% by weight of particles larger than No. 300 mesh B.S.S. (nominal aperture 53 microns). A sample of a commercial deflocculant, being the sodium salt of a polyacrylic acid having a number average molecular weight of 1650, was used as a control. The deflocculants were dispersed in slurries of the kaolinitic clay at a dose rate of 0.3% based on the weight of dry clay. The deflocculated slurries were then tested by measuring the solids content (weight %) required to give a viscosity of 500 c.p. at 22°C. The viscosity at 70% by weight solids content of the slurries was determined on a Brookfield Viscometer, using spindle 3, and a speed of 100 r.p.m. The pH of the suspension was also noted.

The results obtained are set forth in Table I below:

TABLE I

Deflocculant	Solids content (wt.%) at 500 cp.	pH	Viscosity at 70 wt. % solids (cp)
Poly(acrylic acid) (commercial deflocculant)	70.4	6.8	330
Vinyl acetate - acrylic acid (Example 1)	71.0	6.4	260
Vinyl acetate - maleic anhydride (Example 2)	70.1	6.5	430
Vinyl acetate - maleic anhydride (Example 3)	72.1	6.5	166
Vinyl acetate - Methacrylic acid copolymer (Example 4)	70.1	6.5	410
Vinyl chloride - acrylic acid copolymer	70.8	5.0	350

## EXAMPLE 6.

5 The sodium salts of the copolymers prepared in Examples 1 to 4 were tested as deflocculants for a kaolinitic clay containing 70% by weight particles smaller than 2  
 10 microns, 0.7% by weight particles larger than 10 microns, and 0.03% by weight particles larger than No. 300 mesh B.S. sieve. Tetrasodium pyrophosphate was used as a control. The deflocculants were dispersed in slurries of the kaolinitic clay at a dose rate of 0.05% based on the weight of dry clay together with

0.25% by weight of tetrasodium pyrophosphate. The deflocculated slurries were then tested by measuring the solids content (weight %) required to give a viscosity of 500 cp. at 22°C. The viscosity at 70% by weight solids content of the slurries was also determined on a Brookfield Viscometer, using spindle 3, and a speed of 100 r.p.m. These measurements were repeated after the slurries had been standing for 1 hour, 24 hours and 7 days. The pH of the suspension was also determined. The results obtained are set forth in Table II below:

15

20

25

TABLE II

Organic Polymeric Deflocculant	Solids content at 500 cp (wt. %)	pH	Viscosity at 70 wt.% solids (cp)			
			Original	After 1 hour	After 24 hours	After 7 days
NONE (Tetrasodium pyrophosphate only)	71.6	7.6	380	560	>1000	>2000
Vinyl acetate-acrylic acid copolymer (Example 1)	72.7	7.7	185	230	295	314
Vinyl acetate-maleic acid copolymer (Example 2)	71.6	6.9	250	280	350	475
Vinyl acetate-maleic acid copolymer (Example 3)	72.6	7.8	174	185	190	190
Vinyl acetate-methacrylic acid copolymer (Example 4)	71.2	7.4	290	310	370	525

## EXAMPLE 7.

A kaolinitic clay was deflocculated with the sodium salt of the copolymer of Example 3 at a dose rate of 0.05% and tetrasodium pyrophosphate at 0.25% based on the weight of dry clay. The deflocculated slurry was reduced to 60.5 wt. % solids and 16% by weight, based on the weight of dry clay, of a synthetic latex based on a styrene-butadiene copolymer having a solids content of 50 wt. % and a pH of 9.5, was added to give a total solids

content of 60 wt. %. The test was repeated using tetrasodium pyrophosphate at a dose rate of 0.3% by weight based on the weight of dry clay as the deflocculant for the day.

The viscosities of the two mixtures were measured on a Brookfield viscometer using spindle 3 at 100 r.p.m. The viscosity measurements were repeated after the slurries had been standing for 1 hour, 24 hours and 7 days. The results obtained are set forth in Table III below:

TABLE III

Deflocculant	Viscosity (cp) at 60 wt. % solids			
	Original	After 1 hour	After 24 hours	After 7 days
Tetrasodium pyrophosphate (0.3 wt. %)	65	70	110	190
Tetrasodium pyrophosphate (0.25 wt. %) + Vinyl acetate-maleic acid copolymer (Example 3) (0.05 wt. %)	55	55	60	70

## EXAMPLE 8.

The sodium salt of the vinyl acetate-acrylic acid copolymer prepared in Example 1 was used to deflocculate a chalk whiting which was then ground in a ball mill. A commercial deflocculant, obtained as the sodium salt of a polyacrylic acid, was used as a control. It was found that a whiting which had been deflocculated with this copolymer at a dose rate of 0.15 weight % based on the dry chalk whiting could be milled at a solids content of up to 77% by weight, compared with 72% by weight using the control polymer as a deflocculant.

## EXAMPLE 9.

The sodium salts of the copolymers of Examples 2 and 3 were used to deflocculate chalk whiting which was then ground with 10-35 mesh B.S.S. in a sand-grinder of the type disclosed in British Patent Specification No. 1,123,219 which was fitted with a 0.5 H.P. motor. A slurry containing 800 g of dry whiting, at an initial solids content of 70 wt. %, was treated with 0.15 wt. % of each of the

copolymers based on the weight of dry whiting. A sand:whiting ratio of 1.5:1 by weight was used and the chalk whiting was ground for 30 mins. The chalk whiting, which originally contained 30% by weight of particles smaller than 2 microns, was thus ground to give approximately 80% by weight of particles smaller than 2 microns. The ground whiting slurries were passed through a 100 mesh screen to remove the sand. The solids content of the slurries was reduced to a common basis by diluting to 74 wt. %. The viscosity of each slurry was then measured on a Brookfield viscometer using spindle 3 and a speed of 100 r.p.m. The stability of each whiting slurry, in terms of viscosity change with time, was determined at a solids content of 72 wt. %. The results obtained, which are set forth in Table IV below, showed that the effect of optimising the molecular weight distribution of the copolymer, as in Example 3, was to reduce the viscosity of the whiting slurry at a given solids content and to improve the stability of the ground whiting slurry, with respect to viscosity change with time:

TABLE IV

Deflocculant	wt. % <2 $\mu$	Viscosity at 74 wt. % solids (cp)	Viscosity at 72 wt. % solids (cp)			
			Original	After 1 hour	After 24 hours	After 7 days
Vinyl acetate-maleic acid copolymer (Example 2)	78.0	670	340	455	660	620
Vinyl acetate-maleic acid copolymer (Example 3)	80.0	470	145	270	395	375

## EXAMPLE 10.

The sodium salt of the copolymer of Example 3 was used in the preparation of a mixed pigment based on equal parts by weight of a chalk whiting and a kaolinitic clay and in accordance with the method described and claimed in our British Patent Specification No. 1,318,194. The chalk whiting was ground as described in Example 10 above and added to an aqueous dispersion of a kaolinitic clay. The mixed pigment dispersion was then filtered and dried at 80°C.

The dry mixed pigment was then deflocculated in an aqueous slurry with the sodium salt of the copolymer of Example 3 at a dose

rate of 0.1% by weight together with 0.15% by weight of tetrasodium pyrophosphate, both based on the total weight of mixed pigments. The deflocculated slurry was then tested by measuring the solids content (weight %) required to give a viscosity of 500 cp. at 22°C, and by measuring the viscosity of the slurry at 72 wt. % solids as described in Example 10. As a means of estimating the efficiency of the copolymer as a deflocculant, comparative tests were carried out using a commercially available deflocculant, this being the sodium salt of a polyacrylic acid having a number average molecular weight of 1650. The results obtained are set forth in Table V below.

TABLE V

Organic Polymeric Deflocculant	Wt. % CaCO <sub>3</sub> in total pigment	pH	Wt. % solids at 500 cp.	Viscosity at 72 wt. % solids (cp)			
				Original	After 1 hour	After 24 hours	After 7 days
Polyacrylic acid (commercial deflocculant)	49.9	8.6	74.4	205	215	305	850
Vinyl acetate maleic acid copolymer (Example 3)	50.1	8.8	75.0	180	200	330	730

## EXAMPLE 11.

A further batch of the copolymer of vinyl acetate and maleic acid was prepared by the method described in Example 3, but part of the finely divided white powder which precipitated out of solution in xylene was dissolved in methyl alcohol at room temperature. The solution of the copolymer in methyl alcohol was dried at 60°C under vacuum and the resultant glassy solid ground to a fine powder. This fine powder was found by potentiometric titration to require half as much sodium hydroxide for neutralisation as compared with the portion of the copolymer which had not been dissolved in methyl alcohol, thus confirming that a methyl half-ester had been formed. The sodium salt of the esterified copolymer was then used to deflocculate calcite marble which was ground in a sand-grinder which comprised a cylindrical grinding vessel and a central vertical impeller which was driven by

an electric motor at a speed of 1,000 r.p.m. The sand-grinder was charged with 1,500 g of 18—30 B.S.S. sand (0.85—0.50 mm), 700 g of calcite marble all of which passed a No. 300 mesh B.S. sieve (0.053 mm) and 300 ml. of water in which was dissolved 0.45% by weight, based on the weight of calcite marble, of the esterified copolymer deflocculant. The grinding was continued for 1 hour after which time it was found that about 90% by weight of the marble consisted of particles smaller than 2 microns equivalent spherical diameter. The viscosity of suspensions containing respectively 72% and 70% by weight of marble were then measured at 22°C on a Brookfield viscometer using spindle 3 and a speed of 100 r.p.m.

The experiment was then repeated using as the deflocculant the unesterified vinyl acetate-maleic acid copolymer. The results are given in Table VI below:

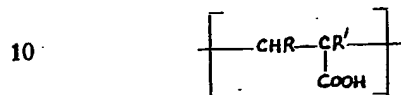
TABLE VI

Deflocculant	Number average mol. wt.	Deflocculant dose (wt. % on marble)	Viscosity (cp) of ground marble	
			72% solids	70% solids
Esterified vinyl acetate-maleic acid copolymer	1610	0.45	90	65
Unesterified vinyl acetate-maleic acid copolymer	1578	0.45	130	85

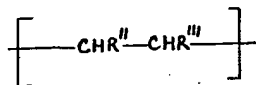
It can be seen that the esterified vinyl acetate-maleic acid copolymer gives an improved performance as compared with the unesterified copolymer.

# WHAT WE CLAIM IS:—

1. A process for deflocculating a particulate material, which comprises adding to a slurry of the particulate material a copolymer, or a water-soluble derivative of a copolymer, having a number average molecular weight in the range of from 700 to 10,000 which contains from 30 to 95 molar percent of a first repeating unit having the general formula



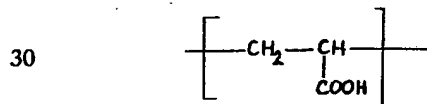
- where R is hydrogen, a lower alkyl group, a carboxylic acid group or a lower alkyl carboxylate ( $-\text{COOAlk}$ ) group and R' is hydrogen or a lower alkyl group; and from 70 to 5 molar percent of a second repeating unit having the general formula



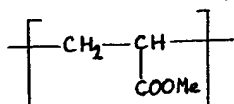
- where R'' is hydrogen or a lower alkyl group and R''' is chlorine, a lower alkyl carboxylic ester ( $-\text{OCOAlk}$ ) group, or a lower alkyl carboxylate ( $-\text{COOAlk}$ ) group.

2. A process according to claim 1, wherein R is hydrogen, a methyl group, a carboxylic acid group or a methyl carboxylate group; R' is hydrogen or a methyl group; R'' is hydrogen; and R''' is chlorine, a methyl carboxylate group, or an acetate group.

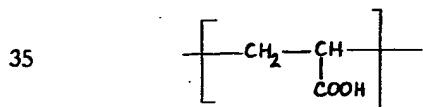
3. A process according to claim 2, wherein said first repeating unit has the formula



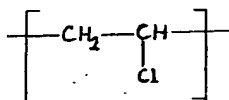
- and second repeating unit has the formula



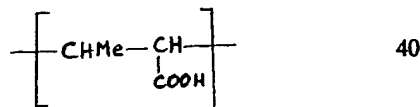
4. A process according to Claim 2, wherein said first repeating unit has the formula



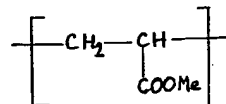
- and second repeating unit has the formula



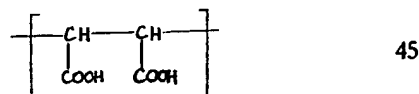
5. A process according to Claim 2, wherein said first repeating unit has the formula



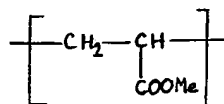
- and second repeating unit has the formula



6. A process according to Claim 2, wherein said first repeating unit has the formula



- and second repeating unit has the formula



7. A process according to any preceding claim, wherein the copolymer has a number average molecular weight in the range of from 1,000 to 5,000.

8. A process according to any preceding claim, wherein said derivative is water-soluble salt.

9. A process according to any one of claims 1 to 7, wherein said derivative is an ester or partial ester.

10. A process according to any preceding claim, wherein said particulate material is a kaolinitic clay.

11. A process according to any one of claims 1 to 9, wherein said particulate material is a calcium carbonate mineral.

12. A process according to any one of claims 1 to 9, wherein said particulate material is a mixture comprising a kaolinitic clay and a calcium carbonate mineral.

13. A process according to any preceding claim, wherein there is added to said slurry from 0.01 to 0.5% by weight, based on the dry weight of the material to be deflocculated, of said copolymer or copolymer-derivative.

14. A process according to claim 13, wherein there is added to said slurry about 0.3% by weight, based on the dry weight of the mineral to be deflocculated, of said copolymer or copolymer derivative.

15. A process according to any preceding claim, wherein an inorganic deflocculant is also added to said slurry.

16. A process according to claim 15, wherein the inorganic deflocculant is tetrasodium pyrophosphate.

17. A process according to claim 16, where-



- 5 in there is added to said slurry about 0.05% by weight of said copolymer or copolymer derivative and about 0.25% by weight of tetrasodium pyrophosphate, both weights based on the dry weight of the material to be deflocculated.
- 10 18. A process according to claim 1 and substantially as described in any one of the foregoing Examples 6 to 11.
- 10 19. A deflocculating composition which includes a copolymer or a copolymer-derivative as defined in any preceding claim.
- 15 20. A composition as claimed in claim 19, which further comprises an inorganic deflocculant.
- 15 21. A composition as claimed in claim 20, wherein said inorganic deflocculant is tetrasodium pyrophosphate.
- 20 22. A deflocculated mineral whenever deflocculated by a process as claimed in any one of claims 1 to 18.

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